

This Page Is Inserted by IFW Operations
and is not a part of the Official Record

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

IMAGES ARE BEST AVAILABLE COPY.

**As rescanning documents *will not* correct images,
please do not report the images to the
Image Problem Mailbox.**

THIS PAGE BLANK (USPTO)



PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

3

In re Application of:

Klaus Hobel; et al

Serial No.: 09/928,616

Filing Date: August 13, 2001

Docket: ACO2814US

Examiner:

For: AQUEOUS CROSS-LINKABLE BINDER
COMPOSTION AND ITS USE IN THE
PRODUCTION OF LACQUER COATINGS

Commissioner of Patents and Trademarks
Washington, D.C. 20231

CERTIFICATE OF MAILING

I hereby certify that this correspondence is being deposited
with the United States Postal Service as First-Class mail in
an envelope addressed to:

Assistant Commissioner for Patents
Washington, DC 20231

On

10/5/01

Angelique Anderson
Angelique Anderson

SUBMISSION OF CERTIFIED COPY OF PRIORITY DOCUMENT

Sir:

Enclosed herewith is a certified copy of European Patent Application No.
00202821.5, filed June 18, 2001 in connection with the above-identified application.

Respectfully submitted,

Joan M. McGillcuddy
Joan M. McGillcuddy
Attorney for Applicants
Reg. No. 35,608

Akzo Nobel Inc.
Intellectual Property Dept.
7 Livingstone Avenue
Dobbs Ferry, New York 10522
(914) 674-5463

THIS PAGE BLANK (USPTO)



Europäisches
Patentamt

European
Patent Office

Office européen
des brevets

5

Bescheinigung

Certificate

Attestation

Die angehefteten Unterla-
gen stimmen mit der
ursprünglich eingereichten
Fassung der auf dem näch-
sten Blatt bezeichneten
europäischen Patentanmel-
dung überein.

The attached documents
are exact copies of the
European patent application
described on the following
page, as originally filed.

Les documents fixés à
cette attestation sont
conformes à la version
initialement déposée de
la demande de brevet
européen spécifiée à la
page suivante.

Patentanmeldung Nr. Patent application No. Demande de brevet n°

00202821.5

Der Präsident des Europäischen Patentamts;
Im Auftrag

For the President of the European Patent Office

Le Président de l'Office européen des brevets
p.o.

I.L.C. HATTEN-HECKMAN

DEN HAAG, DEN
THE HAGUE, 18/06/01
LA HAYE, LE

THIS PAGE BLANK (USPTO)



Europäisches
Patentamt

European
Patent Office

Office européen
des brevets

Blatt 2 der Bescheinigung
Sheet 2 of the certificate
Page 2 de l'attestation

Anmeldung Nr.:
Application no.: 00202821.5
Demande n°:

Anmeldetag:
Date of filing: 11/08/00
Date de dépôt:

Anmelder:
Applicant(s):
Demandeur(s):
Akzo Nobel N.V.
6824 BM Arnhem
NETHERLANDS

Bezeichnung der Erfindung:
Title of the invention:
Titre de l'invention:

Aqueous cross-linkable binder composition and its use in the production of lacquer coatings

In Anspruch genommene Priorität(en) / Priority(ies) claimed / Priorité(s) revendiquée(s)

Staat:
State:
Pays:

Tag:
Date:
Date:

Aktenzeichen:
File no.
Numéro de dépôt:

Internationale Patentklassifikation:
International Patent classification:
Classification internationale des brevets:
C08G18/84, C08G18/08

Am Anmeldetag benannte Vertragsstaaten:
Contracting states designated at date of filing: AT/BE/CH/CY/DE/DK/ES/FI/FR/GB/GR/IE/IT/LI/LU/MC/NL/PT/SE/TR
Etats contractants désignés lors du dépôt:

Bemerkungen:
Remarks:
Remarques:

11-08-2000

ANZU NOBEL PA EP00202821.5

SPEC

ACO 2814 PDEP

AQUEOUS CROSS-LINKABLE BINDER COMPOSITION AND ITS USE IN THE PRODUCTION OF LACQUER COATINGS

5 The invention relates to an aqueous-based cross-linkable binder composition and to its use in the production of lacquer coatings.

Aqueous cross-linkable binder compositions comprising aqueous polyurethane dispersions are well known for the production of film coatings on various substrates such as metal and plastics. Though high-quality coating layers can be obtained with the known aqueous-based binder compositions, the properties of the aqueous polyurethane dispersions used in the known compositions are still a subject for improvement, especially in the field of automotive refinishing shops. Such improvement may concern reducing their excessive foaming when applied via spraying, the amount of organic solvent (VOC), the toxicity of one or more of the components in the binder composition, and/or the curing speed at ambient temperature (RT).

The invention now provides binder compositions which have an acceptable foaming behaviour and cure speed at ambient temperature, which compositions comprise

- (A) an aqueous dispersion of an aldehyde-functional polyurethane having a number average molecular weight of more than 1,000 and an average aldehyde functionality of ≥ 2 , which polyurethane comprises ionic and/or non-ionic dispersing groups, and
- (B) a cross-linker selected from the group of low-molecular weight polyamines and low-molecular weight compounds comprising groups selected from $-\text{CO}-\text{CHR}_1-\text{CO}-$, $\text{NC}-\text{CHR}_1-\text{CO}-$, $\text{NC}-\text{CH}_2-\text{CN}$, $=\text{PO}-\text{CHR}_1-\text{CO}-$, $=\text{CHR}_1-\text{CN}$, $=\text{PO}-\text{CHR}_1-\text{PO}=$, $-\text{CO}-\text{CHR}_1-\text{CN}$, $=\text{PO}-\text{CHR}_1-\text{PO}=$, and $-\text{CO}-\text{CHR}_1-\text{NO}_2$, wherein R_1 has the meaning of hydrogen or a hydrocarbon radical having 1 to 10 carbon atoms.

30 Preference is given to a crosslinker comprising acetoacetate groups.

It should be added that aldehyde-terminated polyurethanes have been disclosed earlier in US-A-3,392,148. The cured resins are said to be useful as protective coatings, mouldings, and adhesives for laminates and the like. The compositions are prepared by the addition reaction of hydroxy-aldehydes with polyisocyanates. The compositions are cured with the aid of an acid catalyst or with a material which will liberate an acid on heating up to about 100-200°C.

Not the slightest allusion is made to the fact that aqueous-based cross-linkable binder compositions curable at ambient temperature can be obtained by starting from an aldehyde-terminated polyurethane having a number average molecular weight of more than 1,000 and an average aldehyde functionality of ≥ 2 which comprises ionic and/or non-ionic dispersing groups, and adding a cross-linker selected from the group of low-molecular weight polyamines and low-molecular weight acetoacetates.

EP-A-0 332 326 discloses an aqueous selfcross-linkable coating composition comprising an aqueous dispersion which comprises at least one polyurethane polymer with hydrazine-functional groups and carbonyl-functional groups. The carbonyl-functional groups may be present in the same polyurethane polymer as the hydrazine-functional groups or not.

EP-A-0 367 051 discloses aqueous storage-stable, carbonyl groups-containing cross-linkable polyurethane dispersions. The carbonyl groups may be derived from hydroxyacetone, hydroxybenzaldehyde, acetoin, benzoin, adducts of diepoxides to ketocarboxylic acids. The polyurethanes are dispersed in water in the presence of ammonia or organic amines such as trialkylamines, e.g. trimethylamine, triethylamine, or hydroxyalkylamines such as trishydroxyethylamine or mixtures thereof. For the cross-linker use is made of polyhydrazides.

EP-A-0 442 852 discloses aqueous coating compositions comprising aqueous polyurethane dispersions in which the polyurethane polymer has chain-pendant or in-chain groups Y with, in all examples, a chain-extending compound having three or more independently reactable enolic carbonyl groups, so that those not taking part in the chain extension will end up as

lateral carbonyl-containing groups in the chain-extended polymer. The only chain-extender compound used in the examples is prepared from trimethylol propane triacetoacetate. Not the slightest allusion is made to the substitution of aldehyde groups for said triacetoacetate groups, or the beneficial effect of such substitution in that when use is made of low-

5 molecular weight polyamines or acetoacetates in the presence of a basic catalyst, the curing reaction may be carried out at ambient temperature. EP-A-0 584 818 discloses an aqueous self-drying and, optionally, cross-linkable coating composition for, e.g., multilayer lacquering of, e.g., repaired
10 cars. The coating composition comprises an aqueous dispersion of a polyurethane resin of number average mol. wt. (Mn) between 2,500 and 1,000,000 containing at least one CH acid group per molecule. The cross-linker comprises an at least 2-functional aldehyde or a free or blocked polyisocyanate with on average 1.5 isocyanate functions per molecule.
15 Preferably, the aldehyde is formaldehyde and/or glyoxal and the polyisocyanate is diisocyanate.

WO 96/41833 discloses a binder composition comprising a strongly activated carbanion-functional polymer and an aldehyde groups-containing cross-linker.

20 The carbanion-functional groups preferably are acetoacetate groups, malonate groups, acetate groups or mixtures thereof. The polymer is an alkyd resin or a polyester resin.

Thus far good results have been obtained with an aqueous-based cross-
25 linkable binder composition when the number average molecular weight of the aldehyde-functional polyurethane is within the range of from 1,000 to 100,000.

Preference is given to a binder composition the polyurethane of which is obtainable by reaction of:

30 —

- a) an organic polyisocyanate,
- b) an organic compound containing at least two isocyanate-reactive groups and having a number average molecular weight in the range of 400 to 6,000,
- 5 c) (an) isocyanate-reactive and/or diisocyanate compound(s) bearing nonionic and/or ionic dispersing groups (or groups which may subsequently be converted to such dispersing groups),
- d) an isocyanate-reactive aldehyde-functional compound,
- e) optionally, an organic polyol having a weight average molecular weight of less than 400, and
- 10 f) optionally, active hydrogen-containing chain extending material.

The polyisocyanate used in making the polyurethane polymer may be an aliphatic, cycloaliphatic or aromatic di-, tri- or tetraisocyanate that may or
 15 may not be ethylenically unsaturated, such as 1,2-propylene diisocyanate, trimethylene diisocyanate, tetramethylene diisocyanate, 2,3-butylene diisocyanate, hexamethylene diisocyanate, octamethylene diisocyanate, 2,2,4-trimethyl hexamethylene diisocyanate, 2,4,4-trimethyl hexamethylene diisocyanate, dodecamethylene diisocyanate, ω,ω' -dipropylether
 20 diisocyanate, 1,3-cyclopentane diisocyanate, 1,2-cyclohexane diisocyanate, 1,4-cyclohexane diisocyanate, isophorone diisocyanate, 4-methyl-1,3-diisocyanatocyclohexane, trans-vinylidene diisocyanate, dicyclohexyl methane-4,4'-diisocyanate, toluene diisocyanate, 1,3-bis(isocyanatomethyl) benzene, xylylene diisocyanate, 1,5-dimethyl-2,4-bis(2-isocyanatoethyl)
 25 benzene, 1,5-dimethyl-2,4-bis(2-isocyanatoethyl) benzene, 1,3,5-triethyl-2,4-bis(isocyanatomethyl) benzene, 4,4'-diisocyanato diphenyl, 3,3'-dichloro-4,4'-diisocyanatodiphenyl, 3,3'-diphenyl-4,4'-diisocyanatodiphenyl, 3,3'-dimethoxy-4,4'-diisocyanatodiphenyl, 4,4'-diisocyanatodiphenyl methane, 3,3'-dimethyl-4,4'-diisocyanatodiphenyl methane,
 30 diisocyanatonaphthalene, the adduct of 2 molecules of a diisocyanate, for example hexamethylene diisocyanate or isophorone diisocyanate, to a diol such as ethylene glycol, the adduct of 3 molecules of hexamethylen

- diisocyanate to 1 molecule of water (available under the trademark Desmodur N of Bayer), the adduct of 1 molecule of trimethylol propan to 3 molecules of toluene diisocyanate (available under the trademark Desmodur L of Bayer), the adduct of 1 molecule of trimethylol propane to 3 molecules of isophorone diisocyanate, compounds such as 1,3,5-triisocyanatobenzene and 2,4,6-triisocyanatotoluene, and the adduct of 1 molecule of pentaerythritol to 4 molecules of toluene diisocyanate. It is preferred that use be made of an aliphatic or cycloaliphatic di- or triisocyanate containing 8-36 carbon atoms.
- 10 Mixtures of polyisocyanates can be used and also polyisocyanates which have been modified by the introduction of urethane, allophanate, urea, biuret, carbodiimide, uretonimine or isocyanurate residues.

- The organic compounds containing at least two isocyanate-reactive groups and having a number average molecular weight in the range of 400 to 6,000 which may be used in the preparation of prepolymers preferably are polymeric organic polyols terminated by hydroxyl groups. The organic polyols particularly include diols and triols and mixtures thereof but higher-functionality polyols may be used, for example as minor components in admixture with diols. The polyols may be selected from the group of polyesters, polyester amides, polyethers, polythioethers, polycarbonates, polyacetals, polyolefins, and polysiloxanes. Preference is given to polyols having a molecular weight in the range of 700 to 3,000.
- 20

- Polyester polyols which may be used include hydroxyl-terminated reaction products of polyhydric alcohols, such as ethylene glycol, propylene glycol, diethylene glycol, neopentyl glycol, 1,4-butanediol, 1,6-hexanediol, furan dimethanol, dimethylol cyclohexane, glycerol, trimethylol propane or pentaerythritol or mixtures thereof with polycarboxylic acids, especially dicarboxylic acids or their ester-forming derivatives, for example succinic, glutaric, and adipic acids, or their dimethyl esters, phthalic anhydride, hexahydrophthalic anhydride or dimethyl terephthalate. Polyesters obtained by the polymerisation of lactones, for example caprolactone, in conjunction
- 25
- 30

with a polyol, may also be used. Polyester amides may be obtained by the inclusion of aminoalcohols such as ethanol amine in the polyesterification mixtures. Suitable polyether polyols include polyC₂(C₃)alkylene oxide glycol and/or polyC₂(C₃)alkylene oxide glycol 1,3-diol, wherein polyC₂(C₃)alkylene oxide stands for polyethylene oxide, optionally comprising propylene oxide units.

Polythioether polyols which may be used include products obtained by condensing thiodiglycol either alone or with other glycols, dicarboxylic acids, formaldehyde, aminoalcohols or aminocarboxylic acids.

Polycarbonate polyols include products obtained by reacting diols, such as 1,3-propane diol, 1,4-butane diol, 1,6-hexane diol, 1,4-cyclohexane dimethanol, diethylene glycol or tetraethylene glycol, with diaryl carbonates, for example diphenyl carbonate, or with phosgene.

Suitable polyolefin polyols include hydroxy-terminated butadiene homo- and copolymers.

Organic polyols having molecular weights below 400 which may optionally be used in the preparation of the polyurethane dispersion particularly include diols and triols and mixtures thereof, but higher-functionality polyols may be used. Examples thereof include ethylene glycol, diethylene glycol, tetraethylene glycol, bis(hydroxyethyl) terephthalate, cyclohexane dimethanol, furan dimethanol, and glycerol.

In order to ensure that the polyurethane is self-dispersible in water, (an) isocyanate-reactive and/or diisocyanate compound(s) bearing nonionic and/or ionic dispersing groups (or groups which may be subsequently converted to such dispersing groups) is/are included as reactant(s) in the preparation of the polyurethane.

Suitable nonionic dispersing groups are the mono C₁-C₄ alkoxy derivatives of the polyether polyols disclosed above. Preferably, the polyurethane comprises 2.5 to 20 wt.% of C₁-C₄ alkoxy polyC₂(C₃)alkylene oxide groups with a number average molecular weight of 500 to 3,000, while preference is given to a polyurethane comprising 5 to 10 wt.% of C₁-C₄ alkoxy

polyC₂(C₃)alkylene oxide groups. Optimum result are obtained with a polyurethane wherein the polyC₂(C₃)alkylene oxide units are polyethylene oxide units.

5 Suitable C₁-C₄ polyC₂(C₃)alkylene oxide compounds contain at least one hydroxyl group. Examples are methoxy polyethylene oxide glycols, methoxy polyethylene oxide-1,3-diols such as Tegomer[®] D-3123 (PO/EO = 15/85; Mn = 1,180), Tegomer[®] D-3409 (PO/EO = 0/100; Mn = 2,240), and Tegomer[®] D-3403 (PO/EO = 0/100; Mn = 1,180) available from Goldschmidt AG, Germany.

10 Suitable ionic dispersing groups are anionic salt groups, e.g., carboxylate, sulphonate and/or phosph(on)ate salt groups which may, e.g., be provided by employing them as a reactant in the polymer formation. Examples of such compounds are carboxy groups containing diols and triols, for example dihydroxy alkanoic acids. Preference is given to 2,2-dimethylol propionic acid.

15 If desired, the carboxy-containing diol or triol may be incorporated into a polyester by reaction with a dicarboxylic acid before incorporation into the polyurethane.

The conversion of any acid groups present in the polyurethane to anionic salt groups may be effected by neutralising said acidic groups before, after (if in combination with nonionic stabilisation) or simultaneously with the formation of an aqueous dispersion of the polymer.

20 As isocyanate-reactive aldehyde-functional compounds may be used hydroxymethyl furfural, 5-hydroxy pentanal, 2,5-dimethyl-2-hydroxy adipaldehyde, 3(β -hydroxyethoxy) propanal, β -hydroxyethoxy acetaldehyde, and the aldol condensation products, such as 3-hydroxybutanal and 3-hydroxy-2-methylpentanal. Thus far optimum results have been obtained with 3,7-dimethyl-7-hydroxyoctanal.

25 Organic polyols having a weight average molecular weight of less than 400 which may optionally be used in the preparation of the polyurethanes include diols and triols and mixtures thereof, but higher-functionality polyols may also be used. Examples of such lower-molecular weight polyols

11-08-2000

A NOBEL PA EP00202821.5

SPEC

8

ACO 2814 PDEP

Include ethylene glycol, diethylene glycol, tetraethylene glycol, bis(hydroxyethyl) terephthalate, cyclohexane dimethanol, furan dimethanol, glycerol, and the reaction products up to molecular weight 400 of such polyols with propylene oxide and/or ethylene oxide.

- 5 As active hydrogen-containing chain extending material compounds bearing groups which are reactive with the free-NCO groups in the polyurethane can be used. The chain extender may be water, but also a polyol, a polyamine or a polythiol.

- The polyurethane dispersions according to the invention may be prepared
- 10 in a conventional manner by reacting a stoichiometric amount or an excess of the organic polyisocyanate with the polymeric organic compound having at least two (terminal) isocyanate-reactive groups (usually hydroxyl) having a molecular weight in the range of 400 to 6,000 with the other required reactants under substantially anhydrous conditions at a temperature
- 15 between about 30°C and about 130°C until the reaction between the isocyanate groups and the isocyanate-reactive (usually hydroxyl) groups is substantially complete. During the production of the isocyanate-terminated prepolymer the reactants are generally used in proportions corresponding to a ratio of isocyanate groups to isocyanate-reactive (usually hydroxyl)
- 20 groups of from about 1:1 to about 6:1, preferably from about 1.5:1 to 3:1. If use is made of a chain extender, the chain extension can be conducted at elevated, reduced or ambient temperatures. Convenient temperatures are from about 5°C to 95°C or, more preferably, from about 10°C to about 45°C.

- 25 Polyurethanes which incorporate chain-pendant aldehyde functionality preferably contain a proportion of aldehyde groups in the polymer within the range of 3 to 200 milli-equivalents, preferably 6 to 100 milli-equivalents, per 100 g of polyurethane polymer.

- 30 Examples of suitable polyamine compounds include non-polymeric polyamine compounds, such as ethylene diamine, propylene diamine, butylen diamine, pentamethylene diamin, hexamethylene diamin,

decamethylene diamine, 4,7-dioxadecane-1,10 diamine, dodecamethylene
diamine, 4,9-dioxadodecane-1,12 diamine, 7-methyl-4,10-dioxatridecane-
1,13 diamine, 1,2-diaminocyclohexane, 1,4-diaminocyclohexane, 4,4'-
diaminodicyclohexyl methane, isophorone diamine, bis(3-methyl-4-
5 aminocyclohexyl) methane, 2,2-bis(4-aminocyclohexyl) propane, nitrile
tris(ethane amine), bis(3-aminopropyl) methylamine, 3-amino-1-
(methylamino) propane, 3-amino-1-(cyclohexyl-amino) propane, N-(2-
hydroxyethyl)-ethylene diamine, and polyamines of the formula $H_2N-(R_2-NH)_n-R_1-NH_2$, wherein the group R_1 and the n groups R_2 may be the same
10 or different and represent an alkylene group containing 2-6 and preferably
2-4 carbon atoms and n is a number from 1-6 and preferably 1-3. The term
alkylene group in this context also refers to a cycloalkylene group or an
alkylene group containing an ether-oxygen atom. Examples of
representative polyalkylene polyamines include diethylene triamine,
15 dipropylene triamine, and dibutylene triamine. It is preferred that these
polyamines be of a (cyclo)aliphatic nature and contain 5-15 carbon atoms,
such as isophorone diamine; more particularly these last polyamines should
contain an α -alkyl group, such as bis(3-methyl-4-aminocyclohexyl) methane
and bis(3-methyl-4-aminocyclohexyl) propane. Other suitable polyamines
20 are the adducts of a (poly)amino compound to a polyfunctional epoxy,
isocyanate, maleinate, fumarate or (meth)acryloyl compound or those
which are obtainable by hydrogenation of polynitro compounds such as
disclosed in EP-B-0678105 or by hydrogenation of polynitriles obtainable by
a Michael addition reaction of for instance polyols or polythiols with
25 acrylonitrile.

Thus far very good results have been obtained when the cross-linker used
was 3-[2,2-bis-(3-amino-propoxymethyl)-butoxy]-propylamine.

Examples of suitable low-molecular weight compounds comprising groups
selected from $-CO-CHR_1-CO-$, $NC-CHR_1-CO-$, $NC-CH_2-CN$, $=PO-CHR_1-$
30 $CO-$, $=CHR_1-CN$, $=PO-CHR_1-PO=$, $-CO-CHR_1-CN$, $=PO-CHR_1-PO=$, and
 $-CO-CHR_1-NO_2$, where in R_1 has the meaning of hydrogen or a
hydrocarbon radical having 1 to 10 carbon atoms, include ketones, such as

acetyl acetone, benzoyl acetone or acetyl dibenzoyl methane, and also esters of an optionally alkyl-substituted acetoacetic acid, such as α -methyl acetoacetic and/or γ -methyl acetoacetic acid, or of acetone dicarboxylic acid, malonic acid units, attached by ester linkage, of malonic acid and monoalkyl derivatives thereof, linear or branched and having 1-6 carbon atoms in the alkyl radical, for example methyl, ethyl, and n-butyl, or phenyl, or esters of cyanoacetic acid with monohydric to hexahydric alcohols containing 1 to 10 carbon atoms. The alkyl-substituted esters, for example α -methyl acetoacetic esters or α,γ -dimethyl acetoacetic esters, contain only one active H atom and therefore are preferably employed in the form of diesters or polyesters of polyhydric alcohols, in order to make available a sufficient number of reactive groups. Examples of alcohols which are suitable for the esterification of the above acids are methanol, ethanol, butanol, and octanol and/or, preferably, polyhydric alcohols.

Further examples of suitable compounds are acetoacetic esters, ethane diol bisacetoacetate, glycerol trimalonate, trimethylol propane triacetoacetate, partial esters of these acids with polyhydric alcohols, as well as the corresponding esters of acrylic resins containing OH groups, polyesters, polyethers, polyester amides, polyester imides, and polyhydroxyl amines, and any nitriles of these acids, for example malonic acid mononitrile or dinitrile, alkoxycarbonyl methane phosphonic acid esters, and the corresponding bismethane phosphonic acid esters.

Preference is given to non-polymeric polyacetoacetate compounds obtainable by reacting diketene or an alkyl acetoacetate with a polyol having two or more hydroxyl groups. These compounds are well known and any of the known compounds can be used. The preferred are those having up to about 50 carbon atoms and the most preferred contain up to about 15 carbon atoms in the molecule. As examples thereof may be mentioned ethylene glycol, propylene glycol, trimethylol propane, 1,2,6-hexane triol, diethylene glycol, 2,2'-dihydroxyphenyl propane, pentaerythritol, polyoxyalkylene polyols formed by the reaction of alkylene oxides with polyhydric alcohols, for example the reaction of ethylene oxide or propylene

- oxide with ethylene glycol; trifunctional products such as those resulting from the reaction of propyl n oxide with glycerol; polycaprolactone polyols such as those resulting from the reaction between propylene glycol and ϵ -caprolactone. Illustrative examples of suitable acetoacetates are trimethylol
- 5 propane triacetoacetate, 1,2,6-hexane triol triacetoacetate, bisacetoacetate of diethylene glycol, bisacetoacetate of 2,2'-bis-4-hydroxyphenyl propane, 1,5-pentanediol diacetoacetate, and pentaerythritol tetracetoacetate.

- The reaction between the aldehyde-functional polyurethane and the low-
- 10 molecular weight cross-linkers comprising groups selected from -CO-CHR₁-CO-, NC-CHR₁-CO-, NC-CH₂-CN, =PO-CHR₁-CO-, =CHR₁-CN, =PO-CHR₁-PO=, -CO-CHR₁-CN, =PO-CHR₁-PO=, and -CO-CHR₁-NO₂, wherein R₁ has the meaning of hydrogen or a hydrocarbon radical having 1 to 10 carbon atoms, is carried out in the presence of a
- 15 basic catalyst having a pK_a \geq 9. Preferred compounds are amines of the amidine type, for example, tetramethyl guanidine, 1,4-dihydropyrimidines, 1,8-diaza-bicyclo[5.4.0]undec-7-ene, 1,4-diaza-bicyclo[2.2.2]octane, 2-alkyl-N-alkyl imidazolines, and adducts of epoxy compounds to tertiary amines such as the reaction product of Epikote 828[®] (ex Shell) with 1,4-diaza-
- 20 bicyclo[2,2,2]octane.

- Other preferred catalysts include quaternary ammonium compounds, for example, quaternary ammonium hydroxides such as tetrabutyl ammonium hydroxide; quaternary ammonium alkoxides such as benzyl trimethyl ammonium methoxide and dilauryl dimethyl ammonium methoxide; and
- 25 quaternary ammonium carbanions such as benzyl trimethyl ammonium acetyl acetate. The amount thereof used varies from 0.05 wt.% to about 6.0 wt.%, preferably from about 0.1 wt.% to about 4.0 wt.%, based upon the combined weight of components (A) and (B).

- 30 The aqueous-based cross-linkable binder composition according to the invention is prepared by dispersing the polyurethane, which is dissolved or dispersed in an organic solvent, in water, followed by evaporation of all or

11-08-2000

ARZU NOBEL PATENTS EP00202821.5

SPEC

12

ACO 2814 PDEP

most of the remaining solvent. The cross-linker may be mixed into the polyurethane solution or dispersion by any suitable technique. However, simply stirring usually is sufficient. Sometimes it may be useful to dilute the solution or dispersion of the binder composition somewhat with an organic solvent like ethyl acetate or 1-methoxy-2-propyl acetate to reduce its viscosity.

Films obtained from these compositions were foam-free at a thickness of $\geq 60 \mu\text{m}$.

For use in coating compositions the binder compositions may further comprise other ingredients, additives or auxiliaries, such as other polymers or polymer dispersions which may or may not contain reactive groups such as epoxy or unsaturated (meth)acrylate groups which can react with one or more of the other binder components, pigments, dyes, emulsifiers (surfactants), pigment dispersion aids, levelling agents, anti-cratering agents, anti-foaming agents, anti-sagging agents, heat stabilisers, UV absorbers, antioxidants, and fillers.

Suitable types of other polymer dispersions include acrylic polymer emulsions and aqueous polyurethane dispersions.

The coating composition of the present invention may be applied to any substrate. The substrate may be, for example, metal, plastic, wood, glass, ceramic, or some other coating layer. The other coating layer may be comprised of the coating composition of the current invention or it may be a different coating composition. The coating compositions of the current invention show particular utility as clear coats, base coats, pigmented top coats, primers, and fillers. The coating compositions can be applied by conventional means such as by spray gun, brush, or roller, spraying being preferred. Curing temperatures preferably are between 0 and 80°C and more preferably between 20 and 60°C. The compositions are particularly suitable in the preparation of coated metal substrates, such as in the refinish industry, in particular the body shop, to repair automobiles and

transportation vehicles, and in finishing large transportation vehicles such as trains, trucks, buses, and aeroplanes.

Preferred is the use of the coating composition of the present invention as a
5 clear coat. Clear coats are required to be highly transparent and must adhere well to the base coat layer. It is further required that the clear coat does not change the aesthetic aspect of the base coat by strike-in, i.e. discolouration of the base coat due to its solvation by the clear coat composition, or by yellowing of the clear coat upon outdoor exposure. A
10 clear coat based on the coating composition of the present invention does not have these drawbacks.

In the case of the coating composition being a clear coat, the base coat may be a conventional base coat known in the coating art. Examples are
15 solvent borne base coats, e.g., Autobase[®] ex Sikkens, based on cellulose acetobutyrate and acrylic resins, and water borne base coats, e.g., Autowave[®] ex Sikkens, based on an acrylic resin dispersion. Furthermore, the base coat may comprise pigments (colour pigments, metallics and/or pearls), wax, solvents, flow additives, neutralising agent, and defoamers.
20 Also high solids base coats can be used. The clear coat composition is applied to the surface of a base coat and then cured. An intermediate curing step for the base coat may be introduced.

The invention will be illustrated with reference to the following examples. Of
25 course these examples are submitted for a better understanding of the invention only; they are not to be construed as limiting in any manner the scope thereof.

In the following examples, the preparation of a number of water borne
30 polyurethane dispersions and binder compositions according to the invention is disclosed. The dispersions were characteris d by th ir solids content, molecular weight, viscosity, and particl size. Th disp rsions'

average particle size was determined with a Coulter LS230 particle size analyzer. The viscosity was determined with a Brookfield CAP 2000 viscometer (LV - 4; 60 revolutions per minute). The solids content was determined in accordance with ASTM method no. 1644-59, with a Sartorius

5 MA 30 moisture analyzer at a temperature of 140°C.

Molecular weight determinations were carried out by gel permeation chromatography on a Waters 2690 instrument, equipped with a Waters 2410 refractive index detector unit and a column type PL1000, available from Polymer Laboratories. Tetrahydrofuran with 0.5 weight% acetic acid
10 served as eluent. The system was calibrated with a polystyrene standard.

Preparation of aldehyde-functional water borne polyurethane dispersions

Polyurethane dispersion 1

- 15 a) a 2-litre 4-neck flask was fitted with a variable speed stirrer, thermocouples in combination with a controller, a distillation column, a condenser, a nitrogen sparge, and a heating mantle. In the flask were placed 836.0 g of hexahydrophthalic anhydride, 962.5 g of 1,6-hexane diol, and 0.45 g of dibutyl tin oxide. The mixture was heated with
20 stirring and under nitrogen flow to 250°C and was kept at this temperature for 4 hours with water being distilled off. Then the mixture was allowed to cool to room temperature. Obtained was a clear, colourless polyester 1a with an acid number of 1.6 mg KOH/g, a hydroxyl number of 179 mg KOH/g, GPC data Mn 990, Mw 1,600.
- 25 b) a 5-litre 4-neck flask was fitted with a variable speed stirrer, thermocouples in combination with a controller, a condenser, a nitrogen inlet and outlet, and a heating mantle. In the flask were placed 71.3 g of isophorone diisocyanate, 54.4 g of a trimer of hexamethylene diisocyanate (Tolonate HDT LV ex Rhodia), 49.1 g of
30 3,7-dimethyl-7-hydroxyoctanal, and 162.8 g of 2-butanone. The mixture was stirred until homogeneous and then 0.19 g tin(II)octanoate was added. The reaction exothermed and was further

11-08-2000

NOBEL PA EP00202821.5

SPEC

15

ACO 2814 PDEP

heated to 80°C and kept at this temperature for 6 hours. After this time, the isocyanate content of the mixture was 7.9%. The reaction mixture was cooled to 30°C, and 46.7 g of polyethylene oxide glycol ($M_n = 1,180$; Tegomer® D3403 ex Tego Chemie Service), 157.8 g of polyester diol 1a, and 4.5 g of dimethylol propionic acid were added to the reaction mixture, followed by the addition of another 0.19 g of tin(II)octanoate. The mixture was heated to 80°C for another 4 hours, after which an isocyanate content below 0.1% was measured. The mixture was cooled to 45°C, and 3.03 g of dimethyl ethanolamine were added. The stirrer was set to the highest speed, and 690 g of water were added at a rate of 10 ml/min. When the addition of water was complete, a distillation head and vacuum pump were connected to the flask and the pressure was gradually lowered until all 2-butanone was distilled off.

A white emulsion with the following characteristics was obtained: Solids content 35 %, M_n 3,310, M_w 19,000, viscosity 36 mPas, pH 8.6, particle size 134 nm.

Polyurethane dispersion 2

- a) In a manner analogous to that disclosed for the preparation of polyurethane dispersion 1, polyester diol 2a was prepared, with the proviso that this time the following ingredients were added: 719.1 g of hexahydrophthalic anhydride, 1064.5 g of dimethylol cyclohexane, and 0.45 g of dibutyl tin oxide. The mixture was heated with stirring and under nitrogen flow to 250°C and was kept at this temperature for 4 hours with water being distilled off. Then the mixture was allowed to cool to room temperature. Obtained was a clear, colourless polyester with an acid number of 0.4 mg KOH/g, a hydroxyl number of 179 mg KOH/g, GPC data M_n 910, M_w 1,430.
- b) in a manner analogous to that disclosed for the preparation of polyurethane dispersion 1, an aldehyde-functional polyurethane

dispersion was prepared, with the proviso that this time the following ingredients were added:

57.9 g of isophorone diisocyanate, 59.7 g of the trimer of isophorone diisocyanate (Vestanat T1890 ex Creanova), 42.2 g of 3,7-dimethyl-7-hydroxyoctanal, and 138.4 g of 2-butanone. The mixture was stirred until homogeneous and then 0.16 g tin(II)octanoate was added. The reaction exothermed and was further heated to 80°C and kept at this temperature for 6 hours. After this time, the isocyanate content of the mixture was 6.9%. The reaction mixture was cooled to 30°C, and 36.6 g of polyethylene oxide glycol ($M_n = 1,180$; Tegomer® D3403 ex Tego Chemie Service), 126.1 g of polyester 2a, and 3.9 g of dimethylol propionic acid were added to the reaction mixture, followed by the addition of another 0.16 g of tin(II)octanoate. The mixture was heated to 80°C for another 4 hours, after which an isocyanate content below 0.1% was measured. The mixture was cooled to 45°C, and 2.58 g of dimethyl ethanolamine were added. The stirrer was set to the highest speed, and 600 g of water were added at a rate of 10 ml/min. When the addition of water was complete, a distillation head and vacuum pump were connected to the flask and the pressure was gradually lowered until all 2-butanone was distilled off.

A white emulsion with the following characteristics was obtained: solids content 36 %, M_n 5,580, M_w 17,800, viscosity 24 mPas, pH 8.3, particle size 159 nm.

25 Preparation of 3-[2,2-bis-(3-amino-propoxymethyl)-butoxy]-propylamine
(polyamine cross-linker)

a) A 1-litre 4-neck flask was fitted with a variable speed stirrer, thermocouples in combination with a controller, a condenser, a nitrogen inlet and outlet, an addition funnel, and a heating mantle. In the flask were placed 48.0 g of trimethylol propane, which was heated to 60°C. Then 0.024 g sodium methoxide was added to the melt. 57.9 g of acrylonitrile were added in 1 hour. The exothermic reaction was

kept between 60 and 70°C by external cooling. After cooling to room temperature traces of precipitate were removed by vacuum filtration. ¹H-NMR analysis of the intermediate product showed a conversion of 97% of all hydroxyl groups. The intermediate had a color of < 1 Gardner.

5 b) Hydrogenation of the intermediate product obtained under a) was carried out in a 2 l stainless steel autoclave with hydrogen and NH₃ dosing equipment, a pitch blade stirrer, and baffles for proper mixing. In the autoclave were placed 201.8 g of a 50 wt.% solution in 2-propanol of the addition product described above and 5 g of Raney Cobalt. Then 15 g of gaseous NH₃ were introduced into the autoclave, which subsequently was heated to 100°C. Hydrogen was then introduced into the reactor to maintain a total pressure of 50 bar. Hydrogenation was continued for 2 hours, during which time the reaction temperature was gradually increased to 150°C. After cooling to room temperature the Cobalt catalyst was removed by filtration and the filtrate was concentrated on a rotary evaporator until all 2-propanol was distilled off.

15 The polyamine was obtained as a liquid with an amine number of 500 mg KOH/g. This liquid was diluted with water to give a clear solution of Gardner colour 2 and a solids content of 50 wt.%.
20

Preparation of the coating compositions

Coating composition A consisted of 20.1 g of polyurethane dispersion 1 and 19.1 g of polyurethane dispersion 2, to which were added 1.3 g of trimethylol propane triacetoacetate, 5.6 g of tetrabutyl ammonium hydroxide (TBAH as a 10% solution in water), and 0.20 g of BYK 346 as wetting agent.

Coating composition B consisted of a mixture of 20.1 g of polyurethane dispersion 1 and 19.1 g of polyurethane dispersion 2, to which were added 2.2 g of the polyamin cross-linker disclosed hereinbefore and 0.21 g of BYK 346 as wetting agent.

Both compositions were applied on tin plated panels in a dry layer thickness of 80 μm (composition A) and 110 μm (composition B), respectively. The panels were allowed to dry at ambient (room) temperature for one day.

- 5 The Persoz Hardness of the obtained coating layers was determined in accordance with French industrial standard method NF T30-016, the result being expressed in seconds.

- 10 The resistance to methylethyl ketone (= 2-butanone) and water was determined after 2 and 7 days of ageing and exposure for one minute (methylethyl ketone) or after 7 days of ageing and exposure for one hour (water).

The properties of the obtained coating layers are given in Table 1.

In the resistance test 0 stands for dissolved, 3 for slightly affected, and 5 for excellent.

All coating layers exhibited excellent water resistance.

15

Table 1

Composition	Persoz Hardness (sec) after ageing during 7 days	Resistance to methylethylketone (MEK) after ageing during		Resistance to water after ageing during 7 days
		2 days	7 days	
A	59	3	3	5
B	34	3	3	5

Claims

1. Aqueous-based cross-linkable binder composition comprising
- 5 (A) an aqueous dispersion of an aldehyde-functional polyurethane having a number average molecular weight of more than 1,000 and an average aldehyde functionality of ≥ 2 , which polyurethane comprises ionic and/or non-ionic dispersing groups, and
- 10 (B) a cross-linker selected from the group of low-molecular weight polyamines and low-molecular weight compounds comprising groups selected from $-\text{CO}-\text{CHR}_1-\text{CO}-$, $\text{NC}-\text{CHR}_1-\text{CO}-$, $\text{NC}-\text{CH}_2-\text{CN}$, $=\text{PO}-\text{CHR}_1-\text{CO}-$, $=\text{CHR}_1-\text{CN}$, $=\text{PO}-\text{CHR}_1-\text{PO}=$, $-\text{CO}-\text{CHR}_1-\text{CN}$, $=\text{PO}-\text{CHR}_1-\text{PO}=$, and $-\text{CO}-\text{CHR}_1-\text{NO}_2$, wherein R_1 has the meaning of hydrogen or a hydrocarbon radical having 1 to 10 carbon atoms.
- 15
2. Aqueous-based cross-linkable binder composition according to claim 1, characterised in that the group $-\text{CO}-\text{CHR}_1-\text{CO}-$ forms part of an acetoacetate group.
- 20
3. Aqueous-based cross-linkable binder composition according to claim 1, characterised in that the number average molecular weight of the aldehyde-functional polyurethane is within the range of from 1,000 to 100,000.
- 25
4. Aqueous-based cross-linkable binder composition according to claim 1, characterised in that the polyurethane is obtainable by reaction of:
- 30 a) an organic polyisocyanate,
- b) an organic compound containing at least two isocyanate-reactive groups and having a number average molecular weight in the range of 400 to 6,000,

- c) (an) isocyanate-reactive and/or diisocyanate compound(s) bearing nonionic and/or ionic dispersing groups (or groups which may subsequently be converted to such dispersing groups),
- d) an isocyanate-reactive aldehyde-functional compound,
- 5 e) optionally, an organic polyol having a weight average molecular weight of less than 400, and
- f) optionally, active hydrogen-containing chain extending material.
5. Aqueous-based cross-linkable binder composition according to claim 1, characterised in that the ionic dispersing group is an anionic dispersing group selected from the group of carboxylate, sulphonate and/or phosph(on)ate salt groups.
- 10 6. Aqueous-based cross-linkable binder composition according to claim 4, characterised in that for the nonionic dispersing group use is made of a C₁-C₄ alkoxy poly C₂-C₃ alkylene-oxide glycol in an amount between 2.5 and 20 wt.%, based on the polyurethane.
- 15 7. Aqueous-based cross-linkable binder composition according to claim 6, characterised in that the C₁-C₄ alkoxy poly C₂-C₃ alkylene-oxide glycol used is C₁-C₄ alkoxy polyethylene oxide glycol in an amount between 5 and 10 wt.%.
- 20 8. Aqueous-based cross-linkable binder composition according to claim 1, characterised in that the aldehyde : acetoacetate equivalent ratio, based on the acetoacetate groups of the low-molecular weight polyacetoacetate and the aldehyde groups of the polyurethane, is within the range of from 0.5:1 to 5:1.
- 25 9. Aqueous-based cross-linkable binder composition according to claim 1, characterised in that the acetoacetate cross-linker is selected from
- 30

the group of trimethylol propane triacetoacetate and trimethylol ethane triacetoacetate.

- 5 10. Aqueous-based cross-linkable binder composition according to claim 1, characterised in that the aldehyde : amino equivalent ratio, based on the primary amino groups of the low-molecular weight polyamine and the aldehyde groups of the polyurethane, is within the range of from 0.5:1 to 5:1.
- 10 11. Aqueous-based cross-linkable binder composition according to claim 1, characterised in that the polyamine cross-linker is selected from the group of α,ω -alkylene diamines having from 2 up to 20 carbon atoms in the alkylene group, cyclohexylene diamine, 2-methyl piperazine, isophorone diamine, adducts of a (poly)amino compound to a polyfunctional epoxy, isocyanate, maleinate, fumarate or 15 (meth)acryloyl compound, and hydrogenated polynitro or polynitrile compounds.
- 20 12. Process for multi-layer lacquer coating of a substrate by applying a base lacquer layer and overcoating with a clear lacquer, characterised in that an aqueous-based cross-linkable binder composition according to claims 1 to 11 is used to produce the base lacquer layer and/or the clear lacquer layer.
- 25 13. Use of the binder compositions according to any one of claims 1 to 11 in the production of clear lacquer coatings.

ABSTRACT

Aqueous-based cross-linkable binder composition comprising

- (A) an aqueous dispersion of an aldehyde-functional polyurethane
5 having a number average molecular weight of more than 1,000 and an
average aldehyde functionality of ≥ 2 , which polyurethane comprises ionic
and/or non-ionic dispersing groups, and
- (B) a cross-linker selected from the group of low-molecular weight
polyamines and low-molecular weight compounds comprising groups
10 selected from $-\text{CO}-\text{CHR}_1-\text{CO}-$, $\text{NC}-\text{CHR}_1-\text{CO}-$, $\text{NC}-\text{CH}_2-\text{CN}$, $=\text{PO}-\text{CHR}_1-$
 $\text{CO}-$,
 $=\text{CHR}_1-\text{CN}$, $=\text{PO}-\text{CHR}_1-\text{PO}=$, $-\text{CO}-\text{CHR}_1-\text{CN}$, $=\text{PO}-\text{CHR}_1-\text{PO}=$, and
 $-\text{CO}-\text{CHR}_1-\text{NO}_2$, wherein R_1 has the meaning of hydrogen or a
hydrocarbon radical having 1 to 10 carbon atoms.
- 15 Preference is given to a coating composition wherein the ionic dispersing
group is an anionic dispersing group selected from the group of
carboxylate, sulphonate and/or phosph(on)ate salt groups, and/or wherein
for the nonionic dispersing group use is made of a C_1-C_4 alkoxy poly C_2-C_3
alkylene-oxide glycol in an amount between 2.5 and 20 wt.%, based on the
20 polyurethane.